

SPECIFICATION

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HIGH FLOW POLYPHENYLENE ETHER FORMULATIONS WITH DENDRITIC POLYMERS

Cross Reference to Related Applications

This application is a continuation of Application No. 09/548,855 filed on April 13, 2000, the entire contents of which are incorporated herein by reference.

Background of Invention

- [0001] This invention relates to polyphenylene ether resins, and more particularly polyphenylene ether formulations with improved flow.
- [0002] Polyphenylene ether resins (PPE) are an extremely useful class of high performance engineering thermoplastics by reason of their hydrolytic stability, high dimensional stability, toughness, heat resistance and dielectric properties. They also exhibit high glass transition temperature values, typically in the range of 150 ° to 210 ° C, and good mechanical performance. This unique combination of properties renders polyphenylene ether based formulations suitable for a broad range of applications, which are well known in the art. One example is injection-molded products, which are used for high heat applications. Polyphenylene ether polymers typically have relatively high molecular weights and possess high melt viscosity with intrinsic viscosity values typically greater than about 0.4 dl/g as measured in chloroform at 25 ° C.
- [0003] One area in which polyphenylene ether based compositions has required an improvement is melt flow capability, i.e. the ability to flow freely at elevated temperatures during various processing stages such as extrusion and molding. Poor melt flow can impact the size and type of the part which can be prepared with the

composition and influence the type of equipment in which the composition is processed. In U.S. Patent No. 4,154,712 to G. Lee Jr. teaches that processability can be improved by decreasing the molecular weight of the polyphenylene ether polymers; however, lower molecular weight sometimes adversely affects other properties such as impact strength. To aid processing, polyphenylene ether resins are often prepared with flow promoters, such as polystyrene, saturated polyalicyclic resins and terpene phenol to reduce viscosity and impart high flow to the resulting composition. Polystyrene, terpene phenol and other such flow promoters reduce the heat deflection temperature (HDT) of the product and typically increase the flammability of the PPE resin, as measured under UL94 standard protocol.

[0004] Efforts to improve the flow characteristics of PPE resins with minimal or no loss of HDT values and impact other properties have been made. For example, U.S. Patent No. 5,081,185 to Haaf et al. describes compositions comprising a blend of two or more polyphenylene ether resins with one resin having high intrinsic viscosity values of at least about 3.8 dl/g and the other having low intrinsic viscosity values of no greater than 0.33 dl/g. The blend of the two PPE resins exhibits higher melt flow with no substantial decrease in heat deflection temperature (HDT) when compared to the high intrinsic viscosity PPE resin of the blend. In addition, U.S. Patent No. 5,376,724 to Bailey et al. discloses polyphenylene ether compositions, which contain a resinous additive that improves flow with only minor reductions in HDT values and impact strength. The resinous additive is said to comprise vinyl aromatic monomers such as styrene monomers or a hydrocarbon compound containing at least 35 wt % aromatic units.

[0005] It is desirable to provide a PPE resin formulation with high flow characteristics with reduced loadings of flow modifier to minimize the impact on HDT values, impact properties and flame retardance.

Summary of Invention

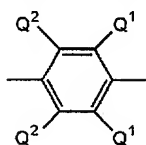
[0006] The present invention provides blends of polyphenylene ether resin, and dendritic polymers. It has been discovered that substantially equivalent improvements in the flow properties of compositions containing polyphenylene ether resins can be obtained with smaller amounts of dendritic polymers when compared to conventional

flow modifying additives.

Detailed Description

[0007] The polyphenylene ether resin preferably has an intrinsic viscosity of at least about 0.35 dl/g, most often in the range of about 0.4–0.6 dl/g, as measured in chloroform at 25 ° C. This polyphenylene ether resin can comprise one or more different polyphenylene ether polymers. The dendritic polymers preferably have a melt viscosity in the range of 1 to 250 Pa at a temperature of 110 ° C and shear rate of 30 sec⁻¹. Preferably, the dendritic polymers are based on polyesters or polyolefins. The compositions of this invention preferably contain at most 15% by weight of the dendritic polymers. The weight ratio of polyphenylene ether resin to the dendritic polymer is preferably greater than 4:1.

[0008] The polyphenylene ether polymers of the polyphenylene ether resins used in compositions of the present invention are known polymers comprising a plurality of aryloxy repeating units preferably with at least 50 repeating units of Formula I



(I)

wherein in each of said units independently, each Q¹ is independently halogen, alkyl (preferably primary or secondary lower alkyl containing up to 7 carbon atoms), aryl (preferably phenyl), halohydrocarbon groups (preferably haloalkyl) having at least two carbons between the halogen atoms and the phenyl nucleus of Formula I, aminoalkyl, hydrocarbonoxy or halohydrocarbonoxy wherein at least two carbon atoms separate the halogen and oxygen atoms and at least two carbon atoms separate the halogen atoms and the phenyl nucleus of Formula I.

[0009]

Each Q² is independently hydrogen, halogen, alkyl (preferably primary or secondary lower alkyl up to 7 carbon atoms), aryl (preferably phenyl), halohydrocarbon (preferably haloalkyl) having at least two carbon atoms between the halogen atoms and the phenyl nucleus of Formula I, hydrocarbonoxy groups or halohydrocarbonoxy groups wherein at least two carbon atoms separate the halogen and oxygen atoms and at least two carbon atoms separate the halogen atoms from the phenyl nucleus of Formula I. Each Q¹ and Q² suitably contains up to about 12

carbon atoms and most often, each Q¹ is an alkyl or phenyl, especially C₁-C₄ alkyl and each Q² is hydrogen.

[0010] The term "polyphenylene ether resin," as used in the specification and claims herein, includes unsubstituted polyphenylene ether polymers, substituted polyphenylene ether polymers wherein the aromatic ring is substituted, polyphenylene ether copolymers and blends thereof. Also included are polyphenylene ether polymers containing moieties prepared by grafting onto the polyphenylene ether in a known manner such materials as vinyl monomers or polymers such as polystyrenes and elastomers, as described in U.S. Patent No. 5,089,566 issued to S. Bruce Brown. Coupled polyphenylene ether polymers in which coupling agents such as low molecular weight polycarbonates, quinones, heterocycles and formals undergo reaction in the known manner with the hydroxy groups of two phenyl ether chains to produce a high molecular weight polymer are also included.

[0011] The polyphenylene ether polymers used in the compositions of this invention may also have various end groups such as amino alkyl containing end groups and 4-hydroxy biphenyl end groups, typically incorporated during synthesis by the oxidative coupling reaction. The polyphenylene ether polymers may be functionalized or "capped" with end groups, which add further reactivity to the polymer and in some instances provide additional compatibility with other polymer systems, which may be used in conjunction with the polyphenylene ether polymers to produce an alloy or blend. For instance, the polyphenylene ether polymer may be functionalized with an epoxy end group, a phosphate end group or ortho ester end group by reacting a functionalizing agent such as 2-chloro-4(2-diethylphosphato epoxy)6-(2,4,6-trimethyl-phenoxy)-1,3,5-trizene, with one of the end groups of the polyphenylene ether polymer, i.e., one of the terminal hydroxyl groups.

[0012] It will be apparent to those skilled in the art from the foregoing that the polyphenylene ether polymers contemplated for use in the present invention include all of those presently known, irrespective of the variations in structural units.

[0013] Specific polyphenylene ether polymers useful in the present invention include but are not limited to poly(2,6-dimethyl-1,4-phenylene ether); poly(2,3,6-trimethyl-1,4-phenylene) ether; poly(2,6-diethyl-1,4-phenylene) ether; poly(2-methyl-6-propyl-

1,4-phenylene) ether; poly(2,6-dipropyl-1,4-phenylene) ether; poly(2-ethyl-6-propyl-1,4-phenylene) ether; poly(2,6-dilauryl-1,4-phenylene) ether; poly(2,6-diphenyl-1,4-phenylene) ether; poly(2,6-dimethoxy-1,4-phenylene) ether; poly(2,6-diethoxy-1,4-phenylene) ether; poly(2-methoxy-6-ethoxy-1,4-phenylene) ether; poly(2-ethyl-6-stearyloxy-1,4-phenylene) ether; poly(2,6-dichloro-1,4-phenylene) ether; poly(2-methyl-6-phenyl-1,4-phenylene) ether; poly(2-ethoxy-1,4-phenylene) ether; poly(2-chloro-1,4-phenylene) ether; poly(2,6-dibromo-1,4-phenylene) ether; poly(3-bromo-2,6-dimethyl-1,4-phenylene) ether; mixtures thereof, and the like.

[0014] Suitable copolymers include random copolymers containing 2,6-dimethyl-1,4-phenylene ether units and 2,3,6-trimethyl-1,4-phenylene ether units.

[0015] The polyphenylene ether resins employed in the compositions of this invention have an intrinsic viscosity greater than about 0.2 dl/g, as measured in chloroform at 25 ° C, and generally have a number average molecular weight within the range of about 3,000 to 40,000 and a weight average molecular weight in the range of 20,000 to 80,000, as determined by gel permeation chromatography.

[0016] The polyphenylether ether polymers suitable for use in this invention may be prepared by any of a number of processes known in the art from corresponding phenols or reactive derivatives thereof. Polyphenylene ether resins are typically prepared by the oxidative coupling of at least one monohydroxy aromatic compound such as 2,6-xyleneol or 2,3,6-trimethylphenol. Catalyst systems are generally employed for such coupling and contain at least one heavy metal compound such as copper, manganese, or cobalt compounds, usually in combination with various other materials. Catalyst systems containing a copper compound are usually combinations of cuprous or cupric ions, halide (e.g., chloride, bromide, or iodide) ions and at least one amine such as cuprous chloride- trimethylamine. Catalyst systems, which contain manganese compounds, are generally alkaline systems in which divalent manganese is combined with such anions as halide, alkoxide or phenoxide. Most often, the manganese is present as a complex with one or more complexing and/or chelating agents such as dialkylamines, alkylenediamines, o-hydroxy aromatic aldehydes, o-hydroxyazo compounds and o-hydroxyaryl oximes. Examples of manganese containing catalysts include manganese chloride-and manganese chloride-sodium

methyrate. Suitable cobalt type catalyst systems contain cobalt salts and an amine.

[0017] Examples of catalyst systems and methods for preparing polyphenylether resins are set forth in U.S. Patent Nos. 3,306,874, 3,306,875, 3,914,266 and 4,028,341 (Hay); U.S. Patent Nos. 3,257,357 and 3,257,358 (Stamatoff); U.S. Patent Nos. 4,935,472 and 4,806,297 (S.B. Brown et al.); and U.S. Patent No. 4,806,602 issued to Dwayne M. White et al.

[0018] In general, the molecular weight of the polyphenylene ether resins can be controlled by controlling the reaction time, the reaction temperature and the amount of catalyst. Longer reaction times will provide a higher average number of repeating units and a higher intrinsic viscosity. At some point, a desired molecular weight (intrinsic viscosity) is obtained and the reaction terminated by conventional means. For example, in the case of reaction systems which make use of a complex metal catalysts, the polymerization reaction may be terminated by adding an acid, e.g., hydrochloric acid, sulfuric acid and the like or a base e.g., potassium hydroxide and the like or the product may be separated from the catalyst by filtration, precipitation or other suitable means as taught by Hay in U.S. Patent No. 3,306,875.

[0019] The term dendritic polymers is used herein refers to both dendrimers and hyperbranched polymers known in the art. Dendrimers and hyperbranched polymers suitable for use in this invention are well defined, highly branched macromolecules that radiate from a central core and are synthesized through a stepwise repetitive branching reaction sequence. Those preferred herein are the star or starburst dendritic polymers having a multifunctional core with radial branching units, which extend from the core. The repetitive branching sequence typically guarantees complete shells for each generation, lending to polymers that are typically monodisperse. The synthetic procedures for dendritic polymer preparation often provide nearly complete control over the size, shape, surface/interior chemistry, flexibility and topology. This invention includes the use of dendritic polymers with complete and symmetrical branches as well as incomplete and asymmetric branches. An example of a suitable synthesis method is to employ a multifunctional compound, such as ethylene diamine, as a core building block. This multifunctional core is first reacted with acrylonitrile to provide a structure with four nitrile groups. These nitrile

groups are reduced to amine units to complete the first cycle. Further reaction cycles prepare dendritic polymers with 8, 16, 32, 64, 128, etc. primary amino groups. The terminal ends of these branching units can be functionalized, if desired, with conventional functional units for dendritic polymers such as hydroxy groups, epoxy groups and ether groups.

[0020] The weight average molecular weight of preferred dendritic polymers can range from about 1,000 to about 21,000 and is preferably from about 1,500 to about 12,000, as determined by gel permeation chromatography. When attempting to increase flow, the most preferred values are at the low end of the molecular weight range of from about 1,500 to about 5,000. Preferably the polymers have a narrow polydispersity of from about 1.3 to about 1.5 and a melt viscosity of 1 to 250 Pa at a temperature of 110 ° C and shear rate of 30 sec⁻¹. The dendritic polymers used in the present invention can optionally be functionalized either in the core or at the periphery of the branching units. Polar groups and non-polar may be bonded to the periphery of the dendritic polymers as desired, depending on the nature of the polyphenylene ether formulation. Preferably, hydroxy and/or epoxy groups are bound at the terminal ends of the dendritic polymers used in this invention.

[0021] The molecules that can be used as a core contain at least one functional group and preferably contain multiple functional groups. These include ammonia, methanol, polymethylene diamines, diethylene triamine, triethylene tetramine, tetraethylene pentamine, linear and branched polyethylene imine, methylamine, hydroxyethylamine, octadecylamine, polyaminoalkylarenes, heterocyclic amines such as imidazolines and piperidines, morpholine, piperazine, pentaerythritol, sorbitol, mannitol, polyalkylenepolyols such as polyethylene glycol and polypropylene glycol, glycols such as ethylene glycol, polyalkylene polymercaptans, phosphine, glycine, thiophenols, phenols, melamine and derivatives thereof such as melamine tris (hexamethylenediamine).

[0022] The branching units can comprise a variety of polymers, which are derived from units typically having two distinct functional groups at different ends. Examples of these simple polymers include polyesters, polyethers, polyolefins, polythioethers, polyamides, polyetherketones, polyalkyleneimines, polyamidoamines,

polyetheramides, polyarylenes, polyalkylenes, aromatic polyalkylenes, polyarylacetylenes and combinations thereof. Examples of suitable dendritic polymers are described in U.S. Patent Nos. 5,530,092 (Meijer et al.); 5,998,565 (Debrabander-Bandenberget al.); 5,418,301 (Hult et al.) and 5,663,247 (Sorensen et al.).

[0023] Preferred dendritic polymers are based on polyesters. Those which are most preferred are the dendritic polymers sold under the trademark BOLTORN[®] available from Perstorp Specialty Chemicals, Perstorp, Sweden. Of this series, BOLTORN H20 and BOLTORN H30 dendritic polymers, which are functionalized with hydroxy groups at the periphery, are preferred and have a weight average molecular weight in the range of about 1,000 to about 4,000.

[0024] Suitable central initiator molecules for the polyester type dendritic polymers include cycloaliphatic or aromatic diols, triols, tetraols, sorbitol, manitol, dipentaerythritol, a monofunctional alcohol and an alkoxylate polymer having a molecular weight less than 2000. Examples of suitable diols include 1,3-propanediol, 1,2-propanediol, 1,3-butanediol, 1,2-ethanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol and polytetrahydrofuran.

[0025] Suitable polyester chain extenders are monofunctional carboxylic acids having at least two hydroxyl groups such as α , α -bis(hydroxymethyl)-propionic acid, α , α -bis(hydroxymethyl)-butyric acid, α , α , α -tris(hydroxymethyl)-acetic acid, α , α -bis(hydroxymethyl)-bularic acid, α , α -bis(hydroxymethyl)-propionic acid, α , β -dihydroxypropionic acid, heptonic acid, citric acid, d- or l- tartaric acid or α -phenylcarboxylic acids such as 3,5-dihydroxybenzoic acid.

[0026] The optional chain terminating agents, which can be used, include saturated monofunctional carboxylic acids, saturated fatty acids, unsaturated monofunctional carboxylic acids, aromatic monofunctional carboxylic acids such as benzoic acid and difunctional or polyfunctional carboxylic acids or anhydrides thereof. An example is behenic acid. Terminal hydroxyl groups in the polyester chain extender can be reacted with chain stoppers with or without functional groups. Suitable polyester-based dendritic polymers are described in U.S. Patent Nos. 5,418,301 and 5,663,247.

[0027] Other suitable chain extenders include aliphatic di, tri or polyhydroxyfunctional

saturated or unsaturated monocarboxylic acids, cycloaliphatic di, tri or polyhydroxyfunctional saturated or unsaturated monocarboxylic acids, aromatic di, tri or polyhydroxyfunctional monocarboxylic acids, aliphatic monohydroxyfunctional saturated or unsaturated di, tri or polycarboxylic acids, cycloaliphatic monohydroxy functional saturated or unsaturated di, tri or polyhydroxycarboxylic acids and aromatic monohydroxy functional di, tri or polycarboxylic acids. The esters of the above acids are also suitable.

[0028] The dendritic polymer is preferably used in the compositions of this invention in an amount, which ranges from about 0.1 to about 15 wt% of the total composition to provide a useful balance of properties. More preferably, an amount of dendritic polymers from about 1 to about 10 wt% of the total composition is used to improve flow and even more preferably, from about 2 to about 6 wt% of the total composition and most preferably from about 2 to about 4 wt% of the total composition is used to improve flow while minimizing the loss of HDT values. Although not preferred, the dendritic polymer can be used in the compositions of this invention in amounts up to 30 wt%.

[0029] The compositions of this invention can be blended with other components in amounts that vary widely. Most often the composition of this invention is employed in an amount in the range of about 5 to 95% by weight with additives and other resins making up the difference. However, this invention includes high flow compositions, which comprise exclusively polyphenylene ether resin and dendritic polymers. Other components, which can be added to the compositions of this invention, include conventional additives and resins conventionally added to PPE formulations.

[0030] Various resins may be blended with the compositions of this invention such as vinyl aromatic resins, polyamides as disclosed in U.S. Patent Nos. 5,981,656 and 5,859,130, polyarylene sulfides as disclosed in U.S. Patent No. 5,290,881, polyphthalamides as disclosed in U.S. Patent No. 5,916,970, polyether amides as disclosed in U.S. Patent No. 5,231,146 and polyesters as disclosed in U.S. Patent No. 5,237,005.

[0031] The vinyl aromatic resins within the compositions of this invention comprise polymers that contain at least 25% by weight of structural units derived from a

monomer of the formula: $(Z)_p - \text{Ph} - \text{C}(\text{R}^3) = \text{CH}_2$ where Ph is phenyl, R^3 is hydrogen, lower alkyl or halogen, Z is vinyl, halogen or lower alkyl and p is 0 to 5. These vinyl aromatic polymers include homopolystyrene, polychlorostyrene, polyvinyltoluene, and rubber-modified polystyrene (sometimes referred to as "HIPS") comprising blends and grafts with elastomeric polymers, as well as mixtures of these materials. Styrene-containing copolymers such as styrene-acrylonitrile copolymers (SAN), styrene-maleic anhydride copolymers, polyalpha-methylstyrene and copolymers of ethylvinylbenzene, divinylbenzene are also suitable.

[0032] The vinyl aromatic polymers are prepared by methods well recognized in the art including bulk, suspension and emulsion polymerization. The amount of vinyl aromatic resin present within the compositions of this invention depends on the properties contemplated and typically ranges from about 5% to 90% by weight, preferably from about 15% to about 60% by weight, based on the weight of the total composition.

[0033] Examples of suitable polystyrene resins are generally known in the art and are described for example in Chapter 3 of Organic Polymer Chemistry, 2nd edition K.G. Saunders, Chapman and Hall, 1988 and in U.S. Patent No. 4,816,510, issued to John B. Yates, III.

[0034] The use of various additives, which may impart a variety of attributes to the compositions of this invention, is also within the scope of this invention. Most additives are well known in the art, as are their effective levels and methods of incorporation. Examples of such additives are impact modifiers, flame retardants, plasticizers, antioxidants, fillers, conductive fillers (e.g., conductive carbon black, carbon fibers, stainless steel fibers, metal flakes and metal powders) reinforcing agents, (e.g., glass fibers), stabilizers (e.g., oxidative, thermal and ultraviolet stabilizers), antistatic agents, lubricants, colorants, dyes, pigments, drip retardants, flow modifiers and other processing aids.

[0035] Materials that enhance the impact strength of the compositions of this invention are not critical but are sometimes desirable. Suitable materials include natural and synthetic elastomeric polymers such as natural rubbers, synthetic rubbers and thermoplastic elastomers. They are typically derived from monomers such as olefins

(e.g., ethylene, propylene, 1-butene, 4-methyl-1-pentene) alkenylaromatic monomers, (e.g., styrene and alphamethyl styrene) conjugated dienes (e.g., butadiene, isoprene and chloroprene) and vinylcarboxylic acids and their derivatives (e.g., vinylacetate, acrylic acid, alkylacrylic acid, ethylacrylate, methyl methacrylate acrylonitrile). They may be homopolymers as well as copolymers including random, block, graft and core shell copolymers derived from these various suitable monomers discussed more particularly below.

[0036] Polyolefins which can be included within the compositions of this invention are of the general structure: $C_n H_{2n}$ and include polyethylene, polypropylene and polyisobutylene with preferred homopolymers being polyethylene, LLDPE (linear low density polyethylene), HDPE (high density polyethylene) and MDPE (medium density polyethylene) and isotactic polypropylene. Polyolefin resins of this general structure and methods for their preparation are well known in the art and are described for example in U.S. Patent Nos. 2,933,480, 3,093,621, 3,211,709, 3,646,168, 3,790,519, 3,884,993, 3,894,999, 4,059,654, 4,166,055 and 4,584,334.

[0037] Copolymers of polyolefins may also be used such as copolymers of ethylene and alpha olefins like propylene and 4-methylpentene-1. Copolymers of ethylene and $C_3 - C_{10}$ monoolefins and non-conjugated dienes, herein referred to as EPDM copolymers, are also suitable. Examples of suitable $C_3 - C_{10}$ monoolefins for EPDM copolymers include propylene, 1-butene, 2-butene, 1-pentene, 2-pentene, 1-hexene, 2-hexene and 3-hexene. Suitable dienes include 1,4 hexadiene and monocyclic and polycyclic dienes. Ratios of ethylene to other $C_3 - C_{10}$ monoolefin monomers can range from 95:5 to 5:95 with diene units being present in the amount of from 0.1 to 10 mol%. EPDM copolymers can be functionalized with an acyl group or electrophilic group for grafting onto the polyphenylene ether as disclosed in U.S. Patent No. 5,258,455.

[0038] Polyolefins are typically present in an amount from about 0.1% to about 10% by weight based on the total weight of the composition. Where the polyolefin is an EPDM, the amount is generally from 0.25% by weight to about 3% by weight of the composition.

[0039] Suitable materials for impact modification include conjugated diene

homopolymers and random copolymers. Examples include polybutadiene, butadiene-styrene copolymers, butadiene-acrylate copolymers, isoprene-isobutene copolymers, chlorobutadiene polymers, butadiene acrylonitrile polymers and polyisoprene. These impact modifiers may comprise from about 1 to 30 weight percent of the total composition.

[0040] A particularly useful class of impact modifiers with conjugated dienes comprises the AB (di-block), $(AB)_m-R$ (di-block) and ABA' (tri-block) block copolymers. Blocks A and A' are typically alkenyl aromatic units and Block B is typically a conjugated diene unit. For block copolymers of formula $(AB)_m-R$, integer m is at least 2 and R is a multifunctional coupling agent for the blocks of the structure AB.

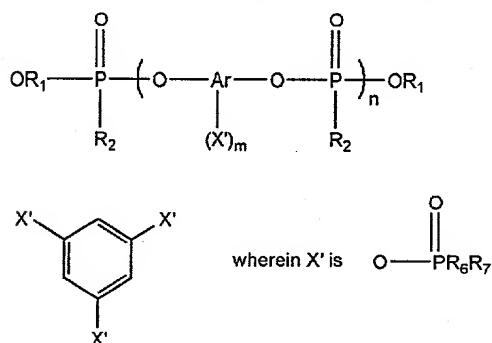
[0041] Also useful are core shell graft copolymers of alkenyl aromatic and conjugated diene compounds. Especially suitable are those comprising styrene blocks and butadiene, isoprene or ethylene-butylene blocks. Suitable conjugated diene blocks include the homopolymers and copolymers described above and they may be partially or entirely hydrogenated by known methods whereupon they may be represented as ethylene-propylene blocks or the like and have properties similar to those of olefin block copolymers. The suitable alkenyl aromatics include styrene, alpha-methyl styrene, para-methyl styrene, vinyl toluene, vinyl xylene and vinyl naphthalene. The block copolymer preferably contains from about 15 to 50% alkenyl aromatic units. Examples of triblock copolymers of this type are polystyrene-polybutadiene-polystyrene (SBS), hydrogenated polystyrene-polybutadiene-polystyrene (SEBS), polystyrene-polyisoprene-polystyrene (SIS) and poly(alpha methylstyrene)-polyisoprene - poly(alpha methylstyrene). Examples of commercially available triblock copolymers are the CARIFLEX[®], KRATON D[®] and KRATON G[®] series from Shell Chemical Company.

[0042] Also included are impact modifiers comprising a radial block copolymer of a vinyl aromatic monomer and a conjugated diene monomer. Copolymers of this type generally comprise about 60 to 95 wt% polymerized vinyl aromatic monomer and about 40 to 5 wt% polymerized conjugated diene monomer. The copolymer has at least three polymer chains, which form a radial configuration. Each chain terminates in a substantially nonelastic segment, to which the elastic polymer segment is joined.

These block copolymers are sometimes referred to as "branched" polymers as described in U.S. Patent No. 4,097,550 and are used in amounts analogous to other conjugated diene based impact modifiers.

[0043] The compositions of this invention can be rendered flame retardant with the use of flame retardant additives known in the art including halosubstituted diaromatic compounds such as 2,2-bis-(3,5-dichlorophenyl)propane, as described in U.S. Patent No. 5,461,096 and phosphorous compounds as described in U.S. Patent No. 5,461,096. Other examples of halosubstituted diaromatic flame retardant additives include brominated benzene, chlorinated biphenyl, brominated polystyrene, chlorine containing aromatic polycarbonates or compounds comprising two phenyl radicals separated by a divalent alkenyl group and having at least two chlorine or two bromine atoms per nucleus, and mixtures thereof.

[0044] The preferred flame retardant compounds employed in the compositions of the present invention are free of halogen. These preferred compounds include phosphorous compounds selected from elemental phosphorous, organic phosphonic acids, phosphonates, phosphinates, phosphinites, phosphine oxides such as triphenylphosphine oxide, phosphines, phosphites and phosphates. Typical of the preferred phosphorous compounds are those of the general formula: $O=P(OZ)_3$, and nitrogen analogs of these phosphorous compounds. Each Z represents the same or different radicals including hydrocarbon radicals such as alkyl, cycloalkyl, aryl, alkyl substituted aryl and aryl substituted alkyl; halogen, hydrogen, and combinations thereof provided that at least one of said Qs is aryl. More preferred are phosphates wherein each Q is aryl. Other suitable phosphates include diphosphates and polyphosphates having the following formulae



wherein Ar is phenyl, biphenyl with a lower alkyl bridge or triphenyl, each R_1 is independently hydrocarbon; R_2 , R_6 and R_7 are independently hydrocarbon or

hydrocarbonoxy, each X^1 is either hydrogen methyl, methoxy or halogen, m is an integer of from 1 to 4; and n is an integer of from about 1 to 30. Preferably, each R_1 is independently phenyl or lower alkyl of from 1 to 6 carbon atoms and R_2 , R_6 and R_7 are each independently phenyl, lower alkyl of 1 to 6 carbon atoms, phenoxy or (lower) alkoxy of from 1 to 6 carbon atoms.

[0045] Examples of suitable phosphates include phenylbisdodecyl phosphate, phenylbisneopentyl phosphate, phenylethylene hydrogen phosphate, phenyl-bis-3,5,5'-trimethylhexyl phosphate, ethyldiphenyl phosphate, 2-ethylhexyl di(p-tolyl), phosphate, diphenyl hydrogen phosphate, bis(2-ethyl-hexyl) p-tolylphosphate, tritolyl phosphate, bis(2-ethylhexyl)-phenyl phosphate, tri(nonylphenyl) phosphate, phenyl-methyl hydrogen phosphate, di(dodecyl) p-tolyl phosphate, tricresyl phosphate, triphenyl phosphate, isopropylated triphenyl phosphate, halogenated triphenyl phosphate, dibutylphenyl phosphate, 2-chlorethyldiphenyl phosphate, p-tolyl bis(2,5,5'-trimethylhexyl) phosphate, 2-ethylhexyldiphenyl phosphate and the like.

[0046] The most preferred phosphates are triphenyl phosphate, the alkylated triphenyl phosphates, including isopropylated and butylated triphenyl phosphates, bis-neopentyl piperidinyl diphosphate, tetraphenyl bisphenol-A diphosphate, tetraphenyl resorcinol diphosphate, hydroquinone diphosphate, bisphenol-A diphosphate, bisphenol-A polyphosphate, mixtures of these compounds and derivatives of these compounds.

[0047] Suitable compounds containing a phosphorus-nitrogen bond include phosphonitrilic chloride, phosphorus ester amides, phosphoric acid amides, phosphonic acid amides, and phosphinic acid amides. Bis-phosphoramide materials derived from piperazine and hydroxyaromatic compounds are especially useful.

[0048] The level of flame retardant added to the compositions of this invention can range from 0.5 to 30 wt%. A preferred level for the phosphorous flame-retardants is from 9% to 17% by weight of the composition. In some embodiments it is preferable to use the phosphorous flame-retardants such as triphenyl phosphate in combination with other flame-retardants such as hexabromobenzene and optionally antimony oxide.

[0049] Suitable phosphorous flame retardant additives are commercially available and methods for preparing the phosphate flame-retardants are generally known in the art. As an example, the compounds may be prepared by reacting a halogenated phosphate compound with various dihydric or trihydric phenolic compounds until the desired number of phosphate functional groups are obtained. Examples of the phenolic compounds are dihydroxy aromatic compounds such as resorcinol and hydroquinone.

[0050] As reinforcing agents, the compositions of the present invention may contain fiber reinforcement such as glass fibers, which greatly increases the flexural strength and modulus as well as the tensile strength of the molded composition obtained therewith. In general, lime-aluminum borosilicate glass that is relatively soda-free ("E" glass) is preferred. Although glass roving may be used, cut fibers are often preferred. The length of such fibers is usually at least 3 mm and a preferred length is in the range of 3 mm to 13 mm. A preferred diameter of the fibers is in the range of about 0.002 mm to about 0.01 mm. The amount of glass fiber employed can range from 0 to 60% by weight of the total composition and is preferably in the range of about 3% to 30% by weight based on the weight of the entire composition. Larger amounts are used where the end use requires a higher degree of stiffness and strength. More preferably, the amount of glass fiber ranges from about 6% to 25% by weight. Carbon fibers, carbon fibrils, Kevlar[®] fibers and stainless steel fibers and metal coated graphite fibers can also be employed at levels of 0 to 60 wt% preferably in the range of 3 to 25 wt%, more preferably in the range of 7% to 10% by weight. Carbon fibers typically have a length of at least 3 mm, preferably from 3 mm to 13 mm. Samples of metal used to coat the graphite fibers include nickel, silver, brass, copper and gold, with nickel being preferred. Fibers and platelets of metals such as aluminum, nickel, iron and bronze are also suitable in amounts up to 60 wt%.

[0051] Suitable non-fibrous inorganic fillers include mica clay, glass beads, glass flakes, graphite, aluminum hydrate, calcium carbonate, silica kaolin, barium sulfate, talcum and calcium silicate (Wollastonite). Effective amounts will differ according to the particular agent used, but they are generally in the range of 0.25 to 60 wt% more typically from 1 to 30 wt% and preferably from 3% to 12% by weight based on the weight of the entire composition. Examples of mica include muscovite, phlogopite, biotite, fluorophlogopite, and synthetic mica. Levels of mica are preferably in the

range of 0.25% to 30% by weight, based on the weight of the entire composition. Preferred amounts of clay range from 0.25% to 30% by weight, based on the weight of the entire composition.

[0052] Suitable pigments include those well known in the art such as TiO_2 , and carbon black. Suitable stabilizers include zinc sulfide, zinc oxide and magnesium oxide.

[0053] While the compositions of this invention preferably are of a reduced viscosity and increased flow, it is contemplated that conventional flow promoters and plasticizers may still be desired for certain embodiments. Examples of suitable flow promoters and plasticizers include the phosphate plasticizers such as cresyl diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, isopropylated and triphenyl phosphate. Chlorinated biphenols and mineral oil are also suitable. When used, the plasticizers are typically employed in an amount of 1–15 wt% based on the weight of the composition.

[0054] Suitable antioxidants include hydroxylamines, hindered phenols such as alkylated monophenols and polyphenols, benzofuranones such as 3-arylbenzofuranone, alkyl and aryl phosphites such as 2,4-di-tert butyl phenol phosphite and tridecyl phosphite, and hindered amines such as dioctyl methylamine oxide and other tertiary amine oxides. Such antioxidants are preferably used in an amount of 0.1 to 1.5 wt%, based on the weight of the composition. Suitable U.V. stabilizers include 4,6-dibenzoyl resorcinols, alkanol amine morpholones and benzotriazole.

[0055] The compositions of this invention may be prepared by well-known procedures. A preferred method of preparation is to first dry blend the polyphenylene ether resin and dendritic polymers and compound the mixture by known techniques such as within an extruder to form a blend. The composition has a reduced viscosity and increased flow as compared to polyphenylene ether resin alone without a significant reduction in HDT values. This composition can be blended with other components or extruded, quenched and chopped into pellets. These pellets can then be melted and molded into articles of a desired shape and size or compounded again to blend with other components before additional processing in preparing finished articles.

[0056] Without further elaboration, it is believed that one skilled in the art can, using the

preceding description, utilize the present invention to its fullest extent. The entire disclosure of all patents, and publications cited above, are herein incorporated by reference.

EXPERIMENTAL

[0057] The examples, comparative examples and controls were prepared by compounding the components identified in Tables 1-4 in a 30 mm Werner and Pfeiderer co-rotating twin screw extruder operating at a temperature of 550 ° F (288 ° C) with a speed of about 350 rpm. The extrudate was quenched with water and pelletized. The pellets were injection molded using a Van Dorn Demag 120 ton injection molding machine (melt temperature 560 ° F (290 ° C) mold temperature 190 ° F (88 ° C)) into various specimens /test bars for UL90 flame out tests, HDT values and various physical properties. The polyphenylene ether was PPO[®] resin (poly(2,6-dimethyl-1,4-phenylene)ether) available from GE Plastics. The polystyrene was GEH1897 high impact polystyrene available from GE Plastics and comprising butadiene rubber. The impact modifier was Kraton[®] D1101 styrene-butadiene-styrene block copolymer, available from Shell Chemical Co. The Boltron[®] H20 and Boltron[®] H30 dendritic polymers were obtained from Perstorp AB, Perstorp Sweden and comprise polyester based dendritic polymers with hydroxy terminal groups. Nirez[®] 2150/7042 flow modifier is a terpene phenol available from Arizona Chemical Co. used in the comparative examples. ZnO and ZnS were used as stabilizers in each formulation. The flame retardant formulations also contained the following: FR-RDP tetraphenyl-resorcinol diphosphate flame retardant, available from Akzo Chemical and Nagase America Co., linear low density polyethylene (LLDPE) available from Millenium Petrochemicals, tridecyl diphosphite (TDP) stabilizer, available from GE Specialty Chemicals and filler Teflon fibrils encapsulated with polystyrene-acrylonitrile (TSAN), available from GE Plastics, Netherlands. The amounts utilized for each formulation appears in Tables 1-4.

[0058]

Heat distortion temperature at 264 psi (1/8 inch) was determined according to the standards in ASTM-D648. Notched Izod was determined by the standards set forth in ASTM-D256 and "Total energy" to failure was determined by standards set forth in ASTM-D3763. Flexural modulus was determined by standards set forth in ASTM-

D790, and tensile strength was determined by standards set forth in ASTM-D638. Five bars were tested for each formulation and the average reported in the Tables except for flexural modulus, where 3 bars were tested and averaged and flammability here 10 bars were tested and averaged for most values. Shear viscosity was measured using a Kayeness capillary rheometer.

COMPARATIVE EXAMPLES A-F and CONTROL X

[0059] Comparative Examples A-F and Control X are set forth in Table 1. Control X contains no flow modifier and Comparative Examples A-F employ Nirez terepene phenol flow modifier.

[t1]

TABLE 1

Formulation	X	A	B	C	D	E	F
.46 IV PPO resin	50	48	44	40	50	50	50
SBS, D1101	5	5	5	5	5	5	5
ZnS	0.1	0.1	0.1	0.1	0.1	0.1	0.1
ZnO	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Nirez 2150/7042		2	6	10	2	6	10
Boltron H20							
Boltron H30							
PS, HIPS GEH 1897	45	45	45	45	43	39	35
HDT @ 264 psi (1/8") °F	245	238	234	235	240	242	251
Notched Izod, 73F ft-lb/in	4.52	4.82	4.94	4.49	4.39	4.38	4.56
Total Energy, 73F ft-lb	39.9	36.4	33.5	31.5	39.9	39.5	34.0
Flexural Modulus, 73F (1/8") kpsi	347	357	340	338	352	349	352
Flexural Str. @ yield, 73F (1/8") psi	13,660	14,130	13,530	13,430	14,670	14,890	15,060
Tensile Str. @ yield, 73F 2 in/m/in, psi	8,230	8,190	7,880	7,730	8,510	8,520	8,660
T. Strength @ break 73F 2 in/m/in, psi	7,240	7,160	6,890	6,680	7,330	7,250	7,230
T. Elongation @ yield, 73F 2 in/m/in, %	3.93	3.89	3.46	3.20	3.84	3.85	3.76
T. Elongation @ break, 73F 2 in/m/in, %	27.6	30.1	29.5	31.3	27.3	26.4	20.5
Kayeness Rheology @ 300C Position, Pa-s							
Rate (1/s)							
100	1009.2	932.2	681.09	515.3	1012.7	858.9	747.6
500	432.4	398.6	307.8	237.5	428.4	382.1	338.2
1000	286.5	262.8	207.3	160.9	281.6	255.7	228.9
1500	222.3	203.1	162.1	126.1	217.4	199.2	179.6

EXAMPLES 1-6 and CONTROL Y

[0060] Examples 1-6 and Control Y are set forth in Table 2. Control Y contains no flow modifier and Examples 1-6 employ BOLTRON H20 dendritic polymer as a flow modifier.

[t2]

TABLE 2

Formulation	Y	1	2	3	4	5
.46 IV PPO resin	50	48	44	40	50	50
SBS, D1101	5	5	5	5	5	5
ZnS	0.1	0.1	0.1	0.1	0.1	0.1
ZnO	0.1	0.1	0.1	0.1	0.1	0.1
Nirez 2150/7042						
Boltron H20		2	6	10	2	6
Boltron H30						
PS, HIPS GEH 1897	45	45	45	45	43	39
HDT @ 264 psi (1/8") °F	248	242	241	232	247	245
Notched Izod, 73F ft-lb/in	4.53	4.80	5.12	NO	4.40	5.60
Total Energy, 73F ft-lb	44.0	42.4	19.1		34.8	13.0
Flexural Modulus, 73F (1/8") kpsi	347	342	320	292	336	323
Flexural Str. @ yield, 73F (1/8") psi	14,840	14,390	13,350	10,670	13,610	13,350
Tensile Str. @ yield, 73F 2 in/m/in, psi	8,460	8,100	7,520	5,810	7,990	8,150
T. Strength @ break 73F 2 in/m/in, psi	7,330	7,080	6,730	5,720	7,010	7,110
T. Elongation @ yield, 73F 2 in/m/in, %	3.86	3.68	3.51	2.40	3.89	3.77
T. Elongation @ break, 73F 2 in/m/in, %	26.8	30.4	25.1	9.6	33.3	36.4
Kayeness Rheology @ 300C Position, Pa-s						
Rate (1/s)						
100	1017.1	764.1	479.9	212.1	776.4	447
500	437.2	343.1	168.9	45.4	353	164.3
1000	289.1	230.3	99.8	26.1	236.2	107.4
1500	223.8	179.7	71.8	19.5	183.5	83.9

EXAMPLES 7-10

[0061]

Examples 7-10 are set forth in Table 3. Examples 7-10 employ BOLTRON H30 dendritic polymer as a flow modifier.

[t3]

TABLE 3

Formulation	7	8	9	10
.46 IV PPO resin	48	44	50	50
SBS, D1101	5	5	5	5
ZnS	0.1	0.1	0.1	0.1
ZnO	0.1	0.1	0.1	0.1
Boltron H30	2	6	2	6
PS, HIPS GEH 1897	45	45	43	39
HDT @ 264 psi (1/8") °F	245	237	246	250
Notched Izod, 73F ft-lb/in	4.40	5.27	4.40	5.42
Total Energy, 73F ft-lb	31.3	14.9	29.2	18.1
Flexural Modulus, 73F (1/8") kpsi	334	314	333	321
Flexural Str. @ yield, 73F (1/8") psi	14,140	12,990	14,270	13,700
Tensile Str. @ yield, 73F 2 in/m/in, psi	7,730	7,400	7,930	8,030
T. Strength @ break 73F 2 in/m/in, psi	6,880	6,680	6,960	7,000
T. Elongation @ yield, 73F 2 in/m/in, %	3.53	3.35	3.83	3.84
T. Elongation @ break, 73F 2 in/m/in, %	31.4	28.3	33.2	33.9
Kayeness Rheology @ 300C Position, Pa-s				
Rate (1/s)				
100	741.9	260.8	803.3	293
500	334.9	94.7	365.8	111.2
1000	225.1	72.5	247.3	84.4
1500	175.7	65.1	193.8	74.7

[0062] A comparison of the data in Table 1 to the data in Tables 2 and 3, shows the addition of dendritic polymer to a polyphenylene ether formulation provides significantly higher reductions in Kayeness rheology at similar loadings to the Nirez 2150/7042 terpene phenol flow modifier. Amounts of dendritic polymer as low as 2 wt show significant effects in reducing viscosity and increasing flow. Heat distortion temperatures do not vary significantly until much higher loadings (10% wt) were introduced. The data also show that impact properties were reduced, but to acceptable levels, particularly at lower concentrations of the dendritic polymer.

EXAMPLES 11-22, COMPARATIVE EXAMPLES G-F and CONTROLS Q and R

[0063] The compositions for Examples 11-22, Comparative examples G-L and Controls Q and R are set forth in Table 4. Examples 11-22 employ either BOLTRON H20 or BOLTRON H30 dendritic polymer as a flow modifier. Comparative examples G-L employ Nirez terpene phenol as an impact modifier and Controls Q and R do not

[t4]

TABLE 4

[illegible][illegible]

27

[0064] The results in Table 4 show that high flow is still obtained with the use of the flame retardant additive and that flammability is at acceptable levels with the addition of the dendritic polymers, particularly at the lower loadings of dendritic polymers.

[0065] The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this

